IMPROVED NON-PYROPHORIC WATER-GAS SHIFT REACTION CATALYSTS

This application is a continuation-in-part of US Serial No. 09/669,044, filed
September 25, 2000, the disclosure of which is herein incorporated by reference as if
fully set forth herein.

The present invention relates to low-pyrophoricity water-gas shift catalysts
having a strong structural support and methods of their use for generating hydrogen by
reaction of carbon monoxide (CO) and water (H_2O) in fluid media, and in particular to
generating hydrogen in a gas stream comprising hydrogen, water, and carbon monoxide.
The catalysts and methods of the invention are useful, for example, in generating
hydrogen in the gas stream supplied to a fuel cell, particularly to proton exchange
membrane (PEM) fuel cells.

Fuel cells directly convert chemical energy into electricity thereby eliminating the
mechanical process steps that limit thermodynamic efficiency, and have been proposed
as a power source for many applications. The fuel cell can be 2 to 3 times as efficient as
the internal combustion engine with little, if any, emission of primary pollutants such as
carbon monoxide, hydrocarbons and nitric oxides. Fuel cell-powered vehicles which
reform hydrocarbons to power the fuel cell generate less carbon dioxide (green house
gas) and have enhanced fuel efficiency.

Fuel cells, including PEM fuel cells [also called solid polymer electrolyte or
(SPE) fuel cells], as known in the art, generate electrical power in a chemical reaction
between a reducing agent (hydrogen) and an oxidizing agent (oxygen) which are fed to
the fuel cells. A PEM fuel cell comprises an anode and a cathode separated by a
membrane which is usually an ion exchange resin membrane. The anode and cathode
electrodes are typically constructed from finely divided carbon particles and proton
conductive resin intermingled with the catalytic and carbon particles. In typical PEM
fuel cell operation, hydrogen gas is electrolytically oxidized to hydrogen ions at the
anode composed of platinum reaction catalysts deposited on a conductive carbon
electrode. The protons pass through the ion exchange resin membrane, which can be a
fluoropolymer of sulfonic acid called a proton exchange membrane. H_2O is produced
when protons then combine with oxygen that has been electrolytically reduced at the
cathode. The electrons flow through an external circuit in this process to do work, for

example, creating an electrical potential across the electrodes. Examples of membrane electrode assemblies and fuel cells are described in US Pat. No. 5,272,017.

Fuel cells require both oxygen and a source of hydrogen to function. The oxygen can be readily obtained in pure form (i.e., O_2) or from the air. However, hydrogen gas is

5   not present in sufficient quantities in the air for fuel cell applications. The low volumetric energy density of isolated hydrogen gas compared to conventional hydrocarbon fuels makes the direct supply of hydrogen gas to fuel cells impractical for most applications because a very large volume of hydrogen gas would be required to provide an equivalent amount of energy stored in a much smaller volume of conventional

10   hydrocarbon fuels such as natural gas, alcohol, oil or gasoline. Accordingly, the conversion of known hydrocarbon based fuel stocks to hydrogen gas is an attractive source of hydrogen for fuel cells and other applications.

Removal of impurities such as sulfur from the starting materials and lowering the concentration of oxidative products generated in the conversion process, such as carbon

15   monoxide, are major challenges in hydrogen production. Fuel cells are generally incapacitated by the presence of even low concentrations of CO, which poisons that catalyst at the anode. Despite development of more CO-tolerant Pt/Ru anodes, fuel cells are still susceptible to compromised function when used with hydrogen sources with a CO concentration above 5 ppm.

20   Current industrial methods for producing high purity hydrogen gas (for example, hydrogen sufficiently free of sulfur and carbon monoxide for use in fuel cell applications) are not practical for fuel cell applications. The production of hydrogen gas from natural hydrocarbon sources is widely practiced in the chemical industry, for example in the production of ammonia and alcohol. A variety of reaction steps

25   employing different carefully designed catalysts are used in the industrial production of hydrogen. A series of several reaction steps is typically required to reduce CO concentrations to below required levels, for example below 5 ppm. Many of these reaction steps require high pressures (for example, in excess of 1,000 psig), high reaction temperatures (for example, in excess of 800 °C) and use self-heating pyrophoric

30   catalysts. The scale and weight of machinery required to safely carry out such processes is too large for many fuel cell applications, such as automobile or residential applications. Furthermore, while the hazards presented by such reaction conditions can

be effectively managed in an industrial production setting, similar hazards present unacceptable levels of risk for most fuel cell applications.

The water-gas shift reaction is a well known catalytic reaction which is used, among other things, to generate hydrogen in a gas-borne stream by chemical reaction of

5   carbon monoxide with water vapor (H_2O) according to the following stoichiometry:

$$CO + H_2O \rightarrow CO_2 + H_2$$

wherein the reaction requires a catalyst. Typical catalysts employed in this reaction are based on combinations of iron oxide with chromium oxides at high temperatures (about 350 °C) or mixtures of copper and zinc materials at lower temperatures (about 200 °C).

10   The currently used commercial water-gas shift (WGS) reaction catalysts have a number of deficiencies when considered for fuel cell applications. Many commercial water-gas shift catalysts are self heating and pyrophoric when exposed to air. For example, high temperature iron-chromium based WGS commercial catalysts in the reduced state undergo a rapid temperature increase of about 400 °C upon exposure to

15   atmospheric air. Similarly, low temperature copper-zinc based WGS commercial catalysts in the reduced state undergo rapid temperature increases of about 750 °C upon exposure to atmospheric air. Exposure of copper oxide WGS reaction catalysts in the reduced state supported on cerium oxides to atmospheric air is known to result in a rapid temperature increase of about 500 to 600 °C and platinum-cerium oxide WGS reaction

20   catalysts can undergo similar temperature increases of about 400 °C. In many cases, such rapid and dramatic temperature increases result in the sintering of the catalyst which can permanently disable the catalyst. Such temperature increases can cause the reduced catalyst to ignite spontaneously when exposed to air. While such materials are practical for industrial synthesis, where reaction conditions can be carefully monitored and

25   appropriate safety controls can be put in place to prevent atmospheric air exposure, many such catalysts pose unacceptably high levels of risk when considered for use in many fuel cell applications in a vehicular or residential setting.

As many materials used in catalysts are expensive, there is also a need for catalysts with comparable or higher activity levels that are more cost effective.

30   Water-gas shift catalysts have been extensively studied. For example, Jacques Barbier and Daniel Duprez, Applied Catalysis B: Environmental 4 (1994) 105-140; "Steam effects in three way catalysts" reviews the water-gas shift reaction using a variety

of catalytic systems, including systems comprising an alumina support, a cerium oxide
promoter and a variety of catalytic metals such as platinum (Pt), rhodium (Rh), and
palladium (Pd).

The oxides of cerium are well known promoters of the WGS reaction. The
promotion of WGS activity of precious metal catalysts by CeO_2 has been described in
the literature in connection with auto exhaust catalysts including, for example, the use of
CeO_2 -impregnated alumina powder as a support in Barbier and Duprez, Applied
Catalysis B: Environmental 3 (1993) 61-83; "Reactivity of steam in exhaust gas catalysis
I: Steam and oxygen/steam conversions of carbon monoxide and of propane over PtRh
catalysts". Such commercially available ceria WGS reaction catalysts are typically in the
form of powders, and are used, for instance, in washcoating monolith supports to form
catalysts for treating automotive exhaust. However, powder based catalysts are not ideal
for other types of applications such as fuel processors in that they lack rigidity, they do
not permit the flow of a gaseous stream of reactants through the catalyst and they often
require large amounts of costly catalytically active metals.

Pyrophoric catalysts have an additional disadvantage. Lengthy and carefully
controlled protocols are necessary to both activate and to passivate (stabilize toward
exposure to air) the catalyst. In addition, these protocols typically require specialized
equipment, such as flow controls, for these processes. Due to the exothermic nature of
the reduction of the copper catalytic agent, activation of typical pyrophoric copper
containing low temperature shift catalysts, for example, requires careful control of both
temperature and the proportion of reducing gas (usually hydrogen) being introduced into
the carrier gas (usually nitrogen or natural gas). In a typical activation procedure, a small
proportion of hydrogen in a carrier gas is initially introduced at lower temperatures. The
temperature of the catalyst bed is then raised incrementally to a higher intermediate
temperature. When this intermediate temperature is reached the proportion of hydrogen
in the carrier gas is incrementally increased. These iterations are repeated until the
catalyst bed is completely reduced. Appropriate precautions must be taken to maintain
the temperature below 230 °C as the copper catalyst begins to sinter above this
temperature. Likewise, appropriate controls and procedures are used to safely discharge
a pyrophoric shift catalyst from a reactor, due to the fact that the oxidation of the copper
catalytic agent is an exothermic process. The catalyst bed requires a passivation step to

safely discharge a reactor. In typical passivation procedures a carrier of an inert gas (typically nitrogen) is used while air is slowly introduced to increase the oxygen level in the carrier gas. The slow, stepwise increase in the proportion of air requires specialized flow controls and monitoring equipment (*Catalyst Handbook Second Edition*; Twigg,

5   M.V., Ed.; Wolfe Publishing, 1989). The protocols and associated equipment required for these activation and passivation methods add to the cost and inconvenience of using pyrophoric low temperature water-gas shift catalysts.

What is needed is a water-gas shift reaction catalyst of significantly lower pyrophoricity upon exposure to atmospheric air, with lower production costs, with at

10   least comparable activity when compared to existing commercial catalysts and in a form that is stable, durable and practical for use with fuel processor applications. The present invention overcomes these deficiencies in the prior art by providing an improved water-gas shift reaction catalyst and methods for the use thereof.

15   ## Summary of the Invention

In one embodiment, the invention relates to a process for carrying out the water-gas shift reaction employing a low-pyrophoricity water-gas shift reaction catalyst. The low-pyrophoricity water-gas shift reaction catalyst has a solid high heat capacity particulate support impregnated with a reducible metal oxide and a catalytic agent. In a

20   preferred process, the water-gas shift reaction catalyst has not more than 50% by weight of the reducible metal oxide. Preferably the reducible metal oxide is in the range of 0.5-35% by weight.

In another preferred process, the particulate support is a high strength support in a durable and rigid form. Preferably, the particulate support is activated alumina, more

25   preferably with a BET effective surface area of at least 10 m^2/g.

In one embodiment of the process, the reducible metal oxide includes one or more of the oxides of Cr, V, Mo, Nd, Pr, Ti, Fe, Ni, Mn, Co, or Ce. Preferably the reducible metal oxide includes one or more of the oxides of Ce, Cr, Fe, or Mn.

In one preferred embodiment of the process, the reducible metal oxide consists of

30   the oxides of Ce.

In another embodiment of the process, the catalytic agent of the low-pyrophoricity water-gas shift reaction catalyst includes one or more of Pt, Pd, Cu, Fe, Rh, or Au or an oxide thereof.

In a preferred embodiment of the process, the catalytic agent is Cu or an oxide thereof. Preferably the copper or an oxide thereof is in the range of 4-20% by weight, calculated as CuO. The high heat capacity support used in this process preferably has alumina particles with a mesh size of 12 or greater. In one preferred process, the

5   reducible metal oxide consists of the oxides of Cr and Ce. In another preferred process, the reducible metal oxide consists of the oxides of Cr. In still another preferred process, the reducible metal oxide consists of the oxides of Ce.

In another preferred embodiment of the process, the catalytic agent is Pt or an oxide thereof. Preferably the high heat capacity support used in this process has alumina

10   particles with a mesh size of 12 or greater. In a preferred embodiment of this process, the reducible metal oxide consists of the oxides of Ce.

In one preferred process for carrying out the water-gas shift reaction, the low-pyrophoricity water-gas shift reaction catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least $10 \ m^2/g$. The low-pyrophoricity

15   water-gas shift reaction catalyst also has up to 25% by weight of an oxide of Ce, calculated as CeO_2, impregnated in the support particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 4 and 14% by weight catalytic agent. The catalytic agent is Cu or an oxide thereof, calculated as CuO. The process for carrying out the water-gas shift reaction has the steps of: a) providing an input gas stream comprising

20   carbon monoxide and water vapor; b) contacting the input gas stream with the low-pyrophoricity water-gas shift reaction catalyst; and c) catalyzing the water-gas shift reaction with the low-pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 1% by volume and about 10% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O. The input gas stream is

25   characterized by a space velocity that is at least 500 hr^{-1} VHSV.

In another preferred process for carrying out the water-gas shift reaction, the low-pyrophoricity water-gas shift reaction catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least $10 \ m^2/g$. The low-pyrophoricity water-gas shift reaction catalyst also has up to 15% by weight of an oxide of chromium,

30   calculated as Cr_2O_3, impregnated in the support particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 4 and 14% by weight catalytic agent. The catalytic agent is copper or an oxide thereof, calculated as CuO. The process for carrying out the water-gas shift reaction has the steps of: a) providing an input gas

stream comprising carbon monoxide and water vapor; b) contacting the input gas stream with the low-pyrophoricity water-gas shift reaction catalyst; and

c) catalyzing the water-gas shift reaction with the low-pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 1% by volume and about 10% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O. The input gas stream is characterized by a space velocity that is at least 500 hr^{-1} VHSV.

In another preferred process for carrying out the water-gas shift reaction, the low-pyrophoricity water-gas shift reaction catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least 10 m^2/g. The low-pyrophoricity water-gas shift reaction catalyst also has up to 25% by weight of an oxide of cerium, calculated as CeO_2 impregnated in the support particles. The low-pyrophoricity water-gas shift reaction catalyst also has up to 10% by weight of an oxide of chromium, calculated as Cr_2O_3, impregnated in the support particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 4 and 14% by weight catalytic agent. The catalytic agent is copper or an oxide thereof, calculated as CuO. The process for carrying out the water-gas shift reaction has the steps of: a) providing an input gas stream comprising carbon monoxide and water vapor; b) contacting the input gas stream with the low-pyrophoricity water-gas shift reaction catalyst; and c) catalyzing the water-gas shift reaction with the low-pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 1% by volume and about 10% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O. The input gas stream is characterized by a space velocity that is at least 500 hr^{-1} VHSV.

In another preferred process for carrying out the water-gas shift reaction, the catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least 10 m^2/g. The low-pyrophoricity water-gas shift reaction catalyst also has up to 25% by weight of an oxide of cerium, calculated as CeO_2, impregnated in the alumina support particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 0.1 and 1.0% by weight of a catalytic agent. The catalytic agent is Pt or an oxide thereof, calculated as Pt. The process for carrying out the water-gas shift reaction has the steps of: a) providing an input gas stream comprising carbon monoxide and water vapor; b) contacting the input gas stream with the low-pyrophoricity water-gas shift reaction catalyst; and c) catalyzing the water-gas shift reaction with the low-

pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 0.1% by volume and about 5% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O. The input gas stream is characterized by a space velocity that is at least 500 hr^{-1} VHSV.

5 In another aspect, the invention relates to an apparatus for carrying out the water-gas shift reaction. The apparatus has a low-pyrophoricity water-gas shift reaction catalyst that has a durable, high heat capacity particulate support impregnated with less than 50% by weight of an oxide of Ce, calculated as CeO_2. The low-pyrophoricity water-gas shift reaction catalyst also has a catalytically effective amount of a catalytic

10 agent. The particulate support has alumina particles with a mesh size of 12 or greater.

In one embodiment of the apparatus, the particulate support of the low-pyrophoricity water-gas shift reaction catalyst is activated alumina with a BET effective surface area of at least 10 m^2/g. In another embodiment of the apparatus, the catalytic agent of the low-pyrophoricity water-gas shift reaction catalyst includes one or more of

15 Pt, Pd, Cu, Fe, Rh, Au or an oxide thereof.

In one preferred apparatus, the low-pyrophoricity water-gas shift reaction catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least 10 m^2/g. The low-pyrophoricity water-gas shift reaction catalyst has up to 25% by weight of an oxide of cerium, calculated as CeO_2, impregnated in the support

20 particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 4 and 14% by weight catalytic agent. The catalytic agent is copper or an oxide thereof, calculated as CuO. An input gas stream contacts the low-pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 1% by volume and about 10% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O.

25 The input gas stream is characterized by a space velocity that is at least 500 hr^{-1} VHSV.

In another preferred apparatus, the low-pyrophoricity water-gas shift reaction catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least 10 m^2/g. The low-pyrophoricity water-gas shift reaction catalyst has up to 15% by weight of an oxide of chromium, calculated as Cr_2O_3, impregnated in

30 the support particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 4 and 14% by weight catalytic agent. The catalytic agent is copper or an oxide thereof, calculated as CuO. An input gas stream contacts the low-pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 1% by volume

and about 10% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O. The input gas stream is characterized by a space velocity that is at least 500 hr^{-1} VHSV.

In another preferred apparatus, the low-pyrophoricity water-gas shift reaction catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least 10 m^2/g. The low-pyrophoricity water-gas shift reaction catalyst has up to 25% by weight of an oxide of cerium, calculated as CeO_2 impregnated in the support particles. The low-pyrophoricity water-gas shift reaction catalyst also has up to 10% by weight of an oxide of chromium, calculated as Cr_2O_3, impregnated in the support particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 4 and 14% by weight catalytic agent. The catalytic agent is copper or an oxide thereof, calculated as CuO. An input gas stream contacts the low-pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 1% by volume and about 10% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O. The input gas stream is characterized by a space velocity that is at least 500 hr^{-1} VHSV.

In another preferred apparatus, the low-pyrophoricity water-gas shift reaction catalyst has alumina support particles with a mesh size of 12 or greater and a BET surface area of at least 10 m^2/g. The low-pyrophoricity water-gas shift reaction catalyst has up to 25% by weight of an oxide of cerium, calculated as CeO_2, impregnated in the alumina support particles. The low-pyrophoricity water-gas shift reaction catalyst also has between 0.1 and 1.0% catalytic agent. The catalytic agent is Pt or an oxide thereof, calculated as Pt. An input gas stream contacts the low-pyrophoricity water-gas shift reaction catalyst. The input gas stream includes: between about 0.1% by volume and about 5% by volume CO, at least 10% by volume hydrogen, and at least 10% by volume H_2O. The input gas stream is characterized by a space velocity that is at least 500 hr^{-1} VHSV.

In another aspect, the invention relates to a low-pyrophoricity water-gas shift reaction catalyst having high heat capacity support particles of a mesh size of 12 or greater impregnated with a reducible metal oxide and a catalytic agent. In one preferred embodiment of the low-pyrophoricity water-gas shift reaction catalyst, the reducible metal oxide includes one or more of the oxides of Cr, V, Mo, Nd, Pr, Ti, Fe, Ni, Mn, Co, or Ce. Preferably the high heat capacity support particles of the low-pyrophoricity water-gas shift reaction catalyst are activated alumina.

In one preferred low-pyrophoricity water-gas shift reaction catalyst, the catalytic agent is Cu or an oxide thereof. Preferably the catalytic agent is in the range of 4-20% by weight, calculated as CuO. In one preferred embodiment the reducible metal oxide of this low-pyrophoricity water-gas shift reaction catalyst consists of the oxides of Ce. In another preferred embodiment, the reducible metal oxide consists of the oxides of Cr. In still another preferred embodiment of this low-pyrophoricity water-gas shift reaction catalyst, the reducible metal oxide consists of the oxides of Cr and Ce.

In a preferred embodiment of the low-pyrophoricity water-gas shift reaction catalyst, the reducible metal oxide is in the range of 0.5-35% by weight.

In another preferred low-pyrophoricity water-gas shift reaction catalyst, the catalytic agent is Pt or an oxide thereof. Preferably the reducible metal oxide of this low-pyrophoricity water-gas shift reaction catalyst consists of the oxides of Ce.

Brief Description of the Drawings

Figure 1 is a graphic representation of test results obtained for the activity and pyrophoricities of various WGS reaction catalysts.

Figure 2 is a graphic representation of test results obtained for the activity and pyrophoricities of Pt/CeO$_2$-containing WGS reaction catalysts.

Figure 3 is a graphic representation of test results related to the dependence of catalytic activity of various WGS reaction catalysts on levels of reducible metal oxide and catalytic agent loadings.

Figure 4 shows a graphic representation of test results obtained related to the dependence of catalytic activity of Pt/CeO$_2$-containing WGS reaction catalysts on levels of reducible metal oxide and catalytic agent loadings.

Figure 5 illustrates comparative data showing the mechanical strength of various catalytic supports.

Figure 6 shows a low-pyrophoricity WGS reaction catalytic device for reducing the CO concentration in a hydrogen gas sample.

Figure 7 is a graphic representation of the effect of the level of Cr$_2$O$_3$ impregnation on the catalytic activity of CuO/Al$_2$O$_3$ low-pyrophoricity WGS reaction catalysts.

Figure 8 is a graphic representation of the effect of the level of chromium oxide impregnation on the catalytic activity of $CuO/CeO_2/Al_2O_3$ low-pyrophoricity WGS reaction catalysts.

Figure 9 illustrates the effect of the order of impregnation of the reducible metal
5   oxide and catalytic agent on the catalytic activity of $CuO/CeO_2/Al_2O_3$ low-pyrophoricity WGS reaction catalysts.

Detailed Description of the Invention

Definitions

10   The definitions of certain terms used herein are as follows:

"activated alumina" means a high BET surface area alumina, for example greater than 10 m^2/g, having primarily one or more of gamma, theta and delta aluminas.

"BET surface area" means the Brunauer, Emmett, Teller method for determining
15   surface area by N_2 adsorption. Unless otherwise specifically stated, all references herein to the surface area refer to the BET surface area.

"catalytically effective amount" means that the amount of material present is sufficient to affect the rate of reaction of the water-gas shift reaction in the sample being treated.

20   "combination" or "combined" when used with reference to a combination of catalyst components means combinations attained by mixtures, impregnation, extrudates or blends of catalyst components, superimposed discrete layers of components and other suitable methods known in the art which can be used to synthesize a catalyst, for example by incorporation of a catalytic agent, one or more metals or metal oxides, and
25   the like on top of or into a support.

"DTA" means differential thermal analysis which is measure of the amount of heat emitted (exotherm) or absorbed (endotherm) by a sample as a function of temperature and/or time.

"gas-borne stream" means a gaseous stream which may contain non-gaseous
30   components such as solid particulates and/or vapors, liquid mist or droplets, and/or solid particulates wetted by a liquid.

"high heat capacity support" means support materials with a heat capacity that is approximately equal to or, preferably, greater than that of the reducible metal oxide in the catalyst.

"incipient wetness impregnation" means the impregnation of the catalyst support
5   with a volume of metal salt solution substantially equal to the pore volume of the support material.

"inlet temperature" shall mean the temperature of the hydrogen, water, and carbon monoxide stream, test gas, fluid sample or fluid stream being treated immediately prior to initial contact of the hydrogen stream, test gas, fluid sample or fluid stream with
10   a catalyst composition.

"low-pyrophoricity" means that an exposure of a reduced catalyst to atmospheric air results in an oxidative temperature rise of not more than 200 °C.

"oxidative temperature rise" means an increase in temperature due to an exothermic oxidation reaction, for example upon exposure of some materials with air.

"percent by volume", "volume percent" or "%v", when used to refer to the
15   amount of a particular gas component of a gas stream, unless otherwise indicated, means the mole percent of the gas component of the gas stream as expressed as a volume percent.

"percent by weight", or "weight percent" or "%wt.", unless otherwise indicated,
20   means weight percent based on the weight of an analyte as a percentage of the total catalyst weight, including the support and any catalytic material impregnated therein, including without limitation the catalytic agent and any metal oxide material. The percent by weight of a particular analyte (e.g reducible metal oxide or catalytic agent) of the catalyst is generally determined after impregnation as a specific oxide with a suitable
25   precursor of the analyte followed by calcination, but before activation of the catalyst.

"product" means a gas or fluid sample, for example a gas stream, such as a hydrogen stream, test gas, fluid sample or fluid stream, after passing through a catalytic region or after having completed all contact with a catalyst composition.

"pyrophoric or pyrophoricity" means that a substance will ignite almost
30   instantaneously after coming into contact with air.

"reactant", "reactant stream" or "input stream" means a gas or fluid sample, for example a gas stream, such as a hydrogen, water , and carbon monoxide stream, test gas,

fluid sample or fluid stream, prior to passing through a catalytic region or prior to initial contact with a catalyst composition.

T(50) means the temperature to achieve 50% conversion of reactant using the catalyst under the specified conditions. T(50) is recognized as a measure of the activity of a catalyst: the lower the T(50), the higher the activity of the catalyst. Unless otherwise specified, T(50) is measured at standard pressure.

"TGA" means thermogravimetric analysis which is measure of the weight change (e.g., loss) of a sample as a function of temperature and/or time.

VHSV means volume hourly space velocity; that is, the flow of a reactant gas in liter per hour per liter of catalyst volume at standard temperature and pressure.

WHSV means weight hourly space velocity; that is, the flow of a reactant gas in liter per hour per kilogram of catalyst.

The present invention provides an improved water-gas shift reaction catalyst and methods for the use thereof, for example, in generating hydrogen from a gas-borne stream. In some embodiments, the present invention provides methods of generating hydrogen in a gas stream or a gas sample using the water-gas shift (WGS) reaction, for instance, generating hydrogen from a gas stream of CO and water in the WGS reaction. In some embodiments, the catalysts of the invention can be used as an intermediate step in a series of chemical processes to generate hydrogen from a gas-borne stream by using the WGS reaction. In some preferred embodiments, the invention provides water-gas shift reaction catalysts and methods for their use, which can significantly reduce the pyrophoric hazard associated with many WGS reaction catalysts upon exposure to atmospheric air. The reduced pyrophoric hazard associated with the catalysts of the invention makes the catalysts more convenient to handle, both in terms of activating and passivating the catalysts. The present invention, in certain embodiments, also provides a water-gas shift reaction catalyst that is durable, and methods of use thereof. For example, the water-gas shift reaction catalysts of the invention are durable in that the catalysts: (i) will typically not undergo sintering upon exposure to atmospheric air, (ii) can be regenerated subsequent to exposure to atmospheric air and (iii) are preferably of a structurally rigid form that is resistant to crumbling and breaking.

The catalysts of the present invention comprise a support impregnated with a reducible metal oxide and a catalytic agent. It has been found, surprisingly, that both the

pyrophoricity of a reducible metal oxide water-gas shift reaction catalyst (e.g., CeO_2-alumina supported catalysts), and the reducible metal oxide loading (e.g., CeO_2 loading) can be lowered while achieving comparable or improved catalytic activity.

5   The catalysts of the invention comprise a structurally strong support of any suitable durable high heat capacity material, such as alumina, which can be in a particulate form having a longest dimension of about 1/32-inch (0.78 mm) to about 1/2 inch (1.25 cm) in cross section. Preferably, the support particle is at least 1/16-inch (1.56 mm) in cross section or has a mesh size of 12 (sieve opening of 1.52 mm) or above. For example, the support particle preferably has a mesh size of 12, 11, 10, etc. The catalytic

10   support can be impregnated with a suitable precursor of a reducible metal oxide such as the oxides of cerium, chromium , or a combination of both, and with a suitable catalytic agent such as Cu or a noble metal such as Pt (or their oxides). Preferred support materials have a heat capacity that is preferably higher than that of the reducible metal oxide. Examples of supports are silica, zeolites, zirconia, titania, zinc oxide and alumina.

15   Activated alumina is a particularly preferred support.

The catalysts of the present invention can take the form of any suitable high strength support such as a particle, pellet, extrudate, tablet and the like. The support is preferably in a durable, rigid form. A number of supports that are suitable for preparing the catalysts of the invention and practicing the methods of the invention are readily

20   commercially available. For example, 1/8-inch diameter alumina particles available from ALCOA as DD-443 (with 327 m^2/g BET surface area measured as received) can be used to practice the invention. Desirable characteristics for preferred supports include having a high mechanical strength (resistance to crumbling), being readily available, the capacity for being impregnated to high loadings with catalytic agents, promoters, metals,

25   metal oxides and the like, and possessing a high heat capacity. Supports with a heat capacity of at least the heat capacity of the reducible metal oxide are preferred. Supports with a heat capacity greater than the heat capacity of the reducible metal oxide are particularly preferred.

Suitable reducible metal oxides include the oxides of Ce, Cr, V, Mo, Nd, Pr, Ti,

30   Fe, Ni, Mn, Co and the like, as well as combinations thereof. Preferred reducible metal oxide include the oxides of cerium. Other preferred reducible metal oxides, particularly with low-temperature water-gas shift catalysts containing copper as a catalytic agent, include the oxides of chromium. The oxides of chromium can be used alone or in

combination with the oxides of cerium in the catalysts of the invention. As is known in the art, the composition of the reducible metal oxide in the catalyst cannot be precisely determined once the catalyst has been activated and is dependent on the reaction conditions in the reactor such as the temperature, pressure, the ratio between the feed

5   material and whether in the presence of a reducing, oxidizing or inert atmosphere. For example, after impregnation of a support with a suitable precursor of cerium oxide (such as $Ce(NO_3)_3$ and calcination, cerium oxide is believed to be present as CeO_2. Once the catalyst is activated and in use in the reactor, however, cerium oxide can be Ce_xO_y where x is 1, 2 or between 1 and 2 and y is 2, 3 or between 2 and 3. Accordingly, as used

10   herein the reducible metal oxides include the reducible metal oxides in these various oxidation states.

Preferably the water-gas shift reaction catalyst has not more than 50 % by weight of the reducible metal oxide. More preferably, the reducible metal oxide is in the range of 0.5-35%wt.

15   The catalytic agent can be any suitable material that is active for the water-gas shift reaction, including but not limited to those currently recognized in the art. Preferably, the catalytic agent is present in the catalyst in a catalytically effective amount for the water-gas shift reaction. In some embodiments, the catalytic agent is preferably combined with a support that has been previously impregnated with a reducible metal

20   oxide. Examples of catalytic agents include Fe, Mn, Co, Ni, Mo, V, Pd, Rh, Au, Os, Ir, Cu, Pt and oxides of these metals as well as combinations thereof. Preferred catalytic agents include Cu and Group VII transition metal elements and certain oxides thereof, and particularly preferred catalytic agents are Pt, Pd and Cu. As understood in the art, some metal catalytic agents may exist in the catalyst in different oxidation states, for

25   example as metal oxides, metal clusters, combinations thereof and the like. As is known in the art, the composition of the catalytic agent in the catalyst cannot be precisely determined once the catalyst has been activated and is dependent on the reaction conditions in the reactor such as the temperature, pressure, the ratio between the feed material and whether in the presence of a reducing or inert atmosphere. For example, a

30   support can be impregnated with a suitable copper precursor, such as $Cu(NO_3)_2$ and calcined to provide a CuO impregnated support. Once activated and in use in a reactor, however, the catalytic agent can be present as Cu, Cu_2O, or CuO. Accordingly, as used herein, the catalytic agent includes the metal itself and all its oxides.

The catalysts of the invention can be prepared by first impregnating the support with the reducible metal oxide precursor, followed by drying and calcination. For example, CeO_2 impregnated alumina support particles can be prepared by incipient wetness impregnation of alumina particles. Accordingly, in a preferred preparation the

5   1/8-inch alumina support particles are first dried and calcined prior to impregnation with the CeO_2 precursor. For example, the alumina support particles can be first dried at ambient temperature, then dried at about 120 °C, then calcined. Next, the calcined 1/8-inch particles are impregnated in an aqueous solution of cerium nitrate (or any other suitable CeO_2 precursor such as cerium acetate, chloride, etc.). The particles are then

10   dried and calcined at 500 °C in air.

After preparation of the solid support with the reducible metal oxide, the support can be impregnated with a precursor of the catalytic agent. For example, incipient wetness impregnation can be used to impregnate a CeO_2 impregnated alumina support (or "CeO_2/alumina particles"), which can be prepared as described above, with a

15   catalytic agent. In some embodiments, a catalytic agent which is Cu or an oxide thereof can be added to CeO_2/alumina particles by impregnation of the CeO_2/alumina particles with Cu-nitrate solution at a weakly acidic pH, dried and calcined to prepare CuO/CeO_2/alumina WGS reaction catalysts. In some embodiments, impregnation of CeO_2/alumina particles with a Pt-nitrate solution, or preferably a water soluble Pt-amine

20   salt solution, is followed by precipitation with acetic acid, drying and calcination to prepare Pt/CeO_2/alumina WGS reaction catalysts of the invention.

In some embodiments, a second reducible metal oxide can be added to the CeO_2/alumina particles before impregnation with a catalytic agent. For example, copper containing catalysts that are well-suited to the low temperature water-gas shift reaction

25   can be prepared in this manner. Impregnation of a CeO_2/Al_2O_3 precursor, with various amounts of a suitable Cr_2O_3 precursor such as a $Cr(NO_3)_3$ solution, followed by drying and calcination can provide $CeO_2/Cr_2O_3/Al_2O_3$ particles. These particles can be impregnated with, for example, a copper nitrate solution followed by drying and calcination to provide a $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalyst. In an alternate preparation, the

30   CeO_2/Al_2O_3 precursor can be impregnated with $Cr(NO_3)_3$ (without a subsequent calcination step) and $Cu(NO_3)_2$ and then calcined together to provide the same $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalyst.

For convenience, the catalytic agents and reducible metal oxides of the catalysts of the invention are described herein as specific oxides to refer to a specific catalyst (e.g. $CuO/Cr_2O_3/CeO_2/Al_2O_3$, $Pt/CeO_2/Al_2O_3$, etc.). The descriptions are believed to reflect the composition of the catalyst after calcination but before activation. As used herein,

5   the percent by weight of the components of the catalyst are determined based on these assumed compositions after calcination but before activation. Once activated and in use, however, the oxidation states of both the catalytic agent and the reducible metal oxide cannot be precisely determined.

Generally, other ingredients may be added to the WGS reaction catalyst of the

10   present invention such as conventional thermal stabilizers for the alumina, e.g., the oxides of lanthanum, barium, silica etc. Thermal stabilization of high surface area cerium oxides and alumina to militate against phase conversion to less catalytically effective low surface area forms is well-known in the art. Thermal stabilizers may be incorporated into the bulk activated alumina, by impregnating the alumina particles with,

15   e.g., a solution of a soluble compound of the stabilizer metal. Such impregnation is then followed by drying and calcining the impregnated particles to convert the soluble stabilizer metal impregnated therein into, for example, a metal oxide.

Figure 1 and **Figure 2** show graphical representations **100** and **200** of some embodiments of the invention. Specifically, the graphs **100** and **200** illustrate that the

20   methods of the invention significantly reduce pyrophoricity of the water-gas shift reaction catalysts without significant loss of WGS reaction catalyst performance compared to water-gas shift reaction catalysts in the prior art.

In **Figure 1** and **Figure 2**, the conversion percentage **110** and **210** of CO to CO_2 by the water-gas shift reaction is shown on the left ordinate (y-axis), temperature **120** and

25   **220** is shown on the abscissa (x-axis), and estimated temperature rise from DTA calculation is shown on the right ordinate axis **130** and **230** in units of °C.

In one embodiment of the invention, the methods of the invention as illustrated in **Figure 1**, can be practiced with WGS reaction catalysts comprising an alumina support impregnated with both a CeO_2 reducible metal oxide and a CuO catalytic agent. A first

30   curve **111** (corresponding to values on the left ordinate axis **110**) represents percent conversion of CO and water to hydrogen and CO_2 and is measured on CO consumed (obtained from water-gas shift reactions performed by the methods of the invention and a

first column **131** (corresponding to values on the right ordinate axis **130**) represents typical oxidative temperature rise associated with low-pyrophoricity water-gas shift reaction catalysts of the invention. A first comparative example is represented by a second curve **112** (corresponding to values on the left ordinate axis **110**), which

5   represents percent conversion of CO to CO_2 obtained from a CuO/CeO_2 water-gas shift reaction catalyst, and by a second column **132** (corresponding to values on the right ordinate axis **130**), which represents typical oxidative temperature rise associated with pyrophoric CuO/CeO_2 water-gas shift reaction catalysts. Comparison of curves **111** and **112** shows that the CuO/CeO_2 impregnated WGS reaction catalysts and methods of the

10   invention provide slightly higher WGS reaction CO conversion between about 150 to 250 °C when compared to CuO/CeO_2 WGS reaction catalysts, but with considerably lower pyrophoricity as measured by oxidative temperature rise (compare columns **131** and **132**).

       The CuO/CeO_2 impregnated WGS reaction catalysts and methods of the

15   invention show a temperature-dependent catalytic activity that is active at lower temperatures than conventional high temperature water-gas shift reaction catalysts (e.g., FeCr), but are active at higher temperatures than conventional low temperature water-gas shift reaction catalysts (e.g., $CuO/ZnO/Al_2O_3$). This can be seen, for example, in the comparative examples presented in **Figure 1**. Specifically, a third curve **113** and a third

20   column **133** show the percent CO conversion and oxidative temperature rise, respectively, for a typical low temperature WGS reaction catalyst, namely $CuO/ZnO/Al_2O_3$. A fourth curve **114** and a fourth column **134** show the percent CO conversion and oxidative temperature rise, respectively, for a typical high temperature WGS reaction catalyst, namely iron-chrome catalysts.

25   Preferred $CuO/CeO_2/Al_2O_3$ catalysts of the invention preferably contain between 4 and 20%wt., more preferably between 4 and 14%wt. of the catalytic agent, calculated as CuO, and up to 25%wt. of an oxide of Ce, calculated as CeO_2.

       In another embodiment of the invention, the methods of the invention as illustrated in **Figure 2**, can be practiced with WGS reaction catalysts comprising an

30   alumina support, preferably an activated alumina support, impregnated with both a CeO_2 reducible metal oxide and a Pt catalytic agent. A first curve **211** (corresponding to values on the left ordinate axis **210**) represents percent conversion of water and CO to

hydrogen and CO_2 and measured on CO consumed obtained from water-gas shift reactions performed by the methods of the invention and a first column **231** (corresponding to values on the right ordinate axis **230**) represents typical oxidative temperature rise associated with low-pyrophoricity water-gas shift reaction catalysts of

5   the invention. A comparative example is represented by a second curve **212** (corresponding to values on the left ordinate axis **210**), which represents percent conversion of CO to CO_2 obtained from a Pt/CeO_2 water-gas shift reaction catalyst, and by a second column **232** (corresponding to values on the right ordinate axis **230**), which represents typical oxidative temperature rise associated with the pyrophoric Pt/CeO_2

10   water-gas shift reaction catalysts. The Pt/CeO_2 WGS reaction catalyst is a pyrophoric WGS reaction catalyst comprising a ceria support combined with a catalytically effective amount of Pt; no alumina is present in the Pt/CeO_2 catalyst. Comparison of curves **211** and **212** shows that these WGS reaction catalysts and methods of the invention provide slightly higher WGS reaction CO conversion between about 200 and 275 °C when

15   compared to Pt/CeO_2 WGS reaction catalysts, but with considerably lower pyrophoricity as measured by oxidative temperature rise (compare columns **231** and **232**).

Preferred $Pt/CeO_2/Al_2O_3$ catalysts of the invention preferably contain between 0.1-1.0%wt. of the catalytic agent, calculated as Pt ,and up to 25%wt. of an oxide of Ce, calculated as CeO_2.

20   To summarize, the WGS reaction catalysts and methods of the invention provide comparable WGS reaction catalytic activity to other WGS reaction catalysts (as shown by comparing curve **111** with curves **112, 113** and **114** and as shown by comparing curves **211** and **212**), but with considerably lower pyrophoricity (as shown by comparing column **131** with columns **132, 133** and **134** and as shown by comparing column **231**

25   with column **232**).

In another embodiment of the invention that is particularly well-suited for the low-temperature water-gas shift reaction, the catalyst comprises alumina support particles impregnated with the reducible metal oxide, Cr_2O_3 and a catalytic agent, CuO (a $CuO/Cr_2O_3/Al_2O_3$ catalyst). As represented in **Figure 7**, the alumina support is

30   impregnated with 8%wt. CuO, and variable amounts of Cr_2O_3, up to 8%wt. The improvement in the catalytic activity at lower temperatures (below 250 °C) with the addition of Cr_2O_3 is seen in **Figure 7**. The CO conversion percentage is shown on the

ordinate and the temperature is shown on the abscissa. In this example, the test gas

composition used was a nitrogen stream containing 8% v CO, 10% v CO_2, 43% v H_2

(dry gas), and 26% v H_2O at a space velocity of 2,500 h^{-1}. A curve **711**, representing the

CO conversion for a catalyst impregnated with only CuO, has a T(50) of approximately

5   214 °C. As represented in the curve **712**, impregnation with 2%wt. of Cr_2O_3 improves

(lowers) the T(50) of the copper catalyst to approximately 173 °C. The T(50) for the

copper catalyst impregnated with 8%wt. Cr_2O_3 is approximately the same (168 °C), as is

seen in curve **713**. In summary the addition of a small amount of Cr_2O_3 results in a

catalyst that has a better catalytic activity as is seen in the significantly lower T(50)'s for

10   these catalysts of the invention.

       Preferred $CuO/Cr_2O_3/Al_2O_3$ catalysts of the invention preferably contain between

4 and 20%wt., more preferably between 4 and 14%wt. of the catalytic agent, calculated

as CuO, and up to 15%wt. of an oxide of chromium calculated as Cr_2O_3.

       A similar improvement in CO conversion at lower temperatures (below 250 °C)

15   is observed in another preferred catalyst for the low-temperature water-gas shift reaction,

a $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalyst. In this embodiment, two reducible metal oxides,

CeO_2 and Cr_2O_3, are impregnated on alumina particles. The effect of impregnating the

alumina particles with Cr_2O_3 already impregnated with 15%wt. CeO_2 and 8%wt. CuO is

illustrated in Figure **8**. The CO conversion percentage is shown on the ordinate and the

20   temperature on the abscissa. A curve **811**, representing the CO conversion percentage

using a catalyst without any impregnated Cr_2O_3 (i.e. a $CuO/CeO_2/Al_2O_3$ catalyst), shows

a T(50) approximately 215 °C. A curve **812**, representing the CO conversion percentage

of a $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalyst impregnated with 2.1%wt. Cr_2O_3, shows the

improved T(50) of approximately 175 °C. The T(50) of a $CuO/Cr_2O_3/CeO_2/Al_2O_3$

25   catalyst impregnated with 5%wt. Cr_2O_3 is approximately the same (172 °C) (curve **813**).

In these $CuO/CeO_2/Al_2O_3$ catalysts of the invention, a lower T(50) is observed for

catalyst prepared by impregnation with small amount of a second metal oxide, Cr_2O_3.

       Preferred $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalysts of the invention preferably contain

between 4 and 20%wt., more preferably between 4 and 14%wt. of the catalytic agent,

30   calculated as CuO, up to 10%wt. of an oxide of chromium calculated as Cr_2O_3, and up to

25%wt. of an oxide of Ce, calculated as CeO_2.

The sequence of synthetic steps to prepare these same $CuO/Cr_2O_3/CeO_2/Al_2O_3$

catalysts of the invention can influence the activity of the catalysts at low temperatures.

The influence is illustrated in **Figure 9**. The CO conversion percentage is shown on the

ordinate and the temperature is shown on the abscissa. In this example, the test gas

composition used was a nitrogen stream containing 8% v CO, 10% v CO_2, 43% v H_2

(dry gas), and 26% v H_2O at a space velocity of 2,500 h^{-1}. All the catalysts whose CO

conversion curves are shown in the graph are prepared from 15%wt. CeO_2 impregnated

alumina (CeO_2/Al_2O_3) particles. After calcining, all the catalysts, whose curves are

shown in the graph, contain 8%wt. CuO. A first curve **911** shows the CO conversion

percentage of a catalyst prepared by: (1) impregnating the CeO_2/Al_2O_3 precursor

particles with $Cr(NO_3)_3$; (2) calcining; (3) impregnation with $Cu(NO_3)_2$; and (4)

calcining. The T(50) for the catalyst prepared in this manner is approximately 180 °C.

A second curve **912** shows the activity of a second catalyst prepared by: (1)

impregnating the CeO_2/Al_2O_3 precursor particles with $Cr(NO_3)_3$; (2) impregnating with

$Cu(NO_3)_2$; and (3) calcining the chromium-cerium impregnated particles in one step (i.e.

without a calcination step after Cr impregnation). The second catalyst in this figure also

has a T(50) of approximately 180 °C. A third catalyst having the same composition but

prepared by: (1) impregnating the CeO_2/Al_2O_3 precursor particles with $Cu(NO_3)_2$; (2)

calcining; (3) impregnating with $Cr(NO_3)_3$; and (4) calcining does not, however, show

the improved activity temperatures below 200 °C (curve **913**). The T(50) for this third

catalyst is approximately 215 °C, or approximately the same as the T(50) (214 °C) for a

copper catalyst prepared without any impregnated Cr_2O_3 (i.e. a $CuO/CeO_2/Al_2O_3$

catalyst) (see curve **914**).

As illustrated in Figures **7** and **8**, the copper catalysts of the invention containing

Cr_2O_3 as a reducible metal oxide, either alone, or in combination with ceria are well-

suited for low temperature water-gas shift reactions. As is understood in the art, low-

temperature water-gas shift reactions are generally conducted below 300 °C, preferably

below 250 °C. The $CuO/Cr_2O_3/Al_2O_3$ catalysts of the invention show a comparable level

of activity for the commercial low temperature Cu/Zn/Al catalysts. The T(50) is about

160 °C as the commercial low temperature $CuO/ZnO/Al_2O_3$ catalysts and approximately

168-177 °C for the catalysts of the invention containing chromium oxides.

The $CuO/Cr_2O_3/Al_2O_3$ and $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalysts of the invention do not have the pyrophoric liability associated with the commercial $CuO/ZnO/Al_2O_3$ catalysts. CuO containing catalyst of the invention exhibit a much lower oxidative temperature rise compared to pyrophoric catalyst such as typical commercial low-

5   temperature shift catalysts (e.g. $CuO/ZnO/Al_2O_3$ catalysts). Pyrophoricity can be measured using a differential scanning calorimeter. An oxidative temperature rise expressed in °K can be calculated for a given catalyst (**Table 6**). Whereas the commercial $CuO/ZnO/Al_2O_3$ catalyst exhibits an oxidative temperature rise of approximately 620 °K, copper containing catalysts of the invention exhibit at least five

10   fold less increase in temperature rise. For example, a $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalyst of the invention (containing 12% CuO, 2% Cr_2O_3, and 5% CeO_2), exhibits approximately 120 °K oxidative temperature rise. Still a more dramatic difference is seen with another $CuO/Cr_2O_3/CeO_2/Al_2O_3$ catalyst of the invention (containing 8% CuO, 2% Cr_2O_3, and 15% CeO_2) which exhibits only an approximately 40 °K oxidative temperature rise.

15   Copper containing catalysts of the invention preferably contain copper and its oxides (calculated as CuO) in a range of 4-20%wt., more preferably 4-14%wt. Preferred copper containing catalysts of the invention suitable for the low-temperature water-gas shift reaction also contain oxides of chromium (calculated as Cr_2O_3), preferably in the range of 0.5-10%wt.

20   Referring now to **Figure 3** and **Figure 4**, the graphs **300** and **400** illustrate that the methods of the invention retain comparable high catalytic activity of conventional water-gas shift catalysts that have higher reducible metal oxide loadings. Even when the WGS reaction catalyst comprises less than 50%wt. loading of the metal oxide and a catalytically effective amount of the catalytic agent, the catalysts of the invention do not

25   show significant loss of catalytic performance compared to water-gas shift catalysts in the prior art.

In **Figure 3** and **Figure 4**, the catalytic agent loading **310** and **410** as a weight percent of the total WGS reaction catalyst (including support, reducible metal oxide and catalytic agent) is shown on the left ordinate (y-axis), the reducible metal oxide loading

30   **320** and **420** is shown as a weight percent of the total catalyst on the abscissa (x-axis), and activity expressed as T(50) is shown on the right ordinate axis **330** and **430** in units of °C.

Turning to **Figure 3**, in one embodiment of the invention, the methods of the invention can be practiced with WGS reaction catalysts comprising an alumina support impregnated with both a CeO_2 reducible metal oxide and a CuO catalytic agent. A first series of curves **331**, **332**, **333**, and **334** (corresponding to values on the right ordinate axis **330**) represent activity of the water-gas shift reaction catalyst of the methods of the invention and measured by T(50), for four different reducible metal oxide loadings **321**, **322**, **323** and **324**. Under each curve **331**, **332**, **333** and **334**, there is a set of three columns corresponding to values on the left ordinate axis **310** and labeled with a corresponding number and letter ("a", "b" or "c") designation (specifically, columns **311a**, **311b**, **311c**, **312a**, **312b**, **312c**, **313a**, **313b**, **313c**, **314a**, **314b** and **314c**). For example columns **311a**, **311b** and **311c** are under curve **331**. Each column represents the catalytic agent loading in the catalyst as a weight percent of the total catalyst, and as read on the left ordinate axis **310**. Each data point on each curve corresponds to the T(50) activity for the catalytic agent loading of the column underneath it. For example, in one embodiment, a WGS reaction catalyst with a 5%wt. CeO_2 loading **321** and a 12 % CuO loading **311a** in an alumina support corresponds to a T(50) temperature of about 200 °C (reading curve **331**). Likewise, in one embodiment, a WGS reaction catalyst with a 20%wt. CeO_2 loading **324** and an 8%wt. CuO loading **314b** in an alumina support corresponds to a T(50) temperature of about 225 °C (reading curve **334**).

Figure 4 illustrates another embodiment of the invention wherein the low-pyrophoricity WGS reaction catalyst is an alumina support impregnated with a CeO_2 reducible metal oxide and with a Pt catalytic agent. The curve **431** (corresponding to values on the right ordinate axis **430**) represents the activity of the water-gas shift reaction catalyst measured by T(50) for two different reducible metal oxide loadings **421** and **422**. Under the curve **431**, there are two columns, **411** and **412**. Each column represents the catalytic agent loading in the WGS reaction catalyst as a weight percent of the total WGS reaction catalyst, and as read on the left ordinate axis **410**. Each data point on each curve corresponds to the T(50) activity for the catalytic agent loading of the column underneath it. For example, in one embodiment, a WGS reaction catalyst comprising 13%wt. CeO_2 loading **421** and a 0.37% Pt loading **411** in an alumina support corresponds to a T(50) temperature of about 260 °C (reading curve **431**). Similarly, in one embodiment, a WGS reaction catalyst comprising a 24%wt. CeO_2 loading **422** and a

0.7% Pt loading **412** in an alumina support corresponds to a T(50) temperature of about 255 °C (reading curve **431**).

For low-pyrophoricity $CuO/CeO_2/Al_2O_3$ WGS catalysts, one skilled in the art would recognize that for the catalyst illustrated in **Figure 3**, a catalytically effective amount of the catalytic agent (CuO) of between about 4%wt. and 12%wt. by weight, depending on the reducible metal oxide loading, is desirable to maximize catalytic activity.

Significantly, the catalytic activity for low-pyrophoricity WGS reaction catalysts with reducible metal oxide (CeO_2) loadings of less than 25%wt. is comparable to or higher than the catalytic activity of pyrophoric WGS reaction catalysts that contain higher amounts of reducible metal oxide. For example, low-pyrophoricity WGS reaction $CuO/CeO_2/Al_2O_3$ catalysts with catalytically effective loadings of a catalytic agent (CuO) corresponding to columns **311b**, **311c**, **312a**, **312b**, **313b**, **313c**, **314b**, and **314c** all have reducible metal oxide (CeO_2) loadings of less than 25%wt. and retain a WGS reaction catalytic activity shown by curves **331**, **332**, **333**, and **334**.

Comparable levels of WGS catalytic activity for low-pyrophoricity WGS reaction catalysts ($CuO/CeO_2/Al_2O_3$) and pyrophoric (CuO/CeO_2) WGS reaction catalysts can be seen in **Figure 1**. The catalytic activity (represented by curve **111**) of the low-pyrophoricity WGS catalyst, having a CeO_2 content of 20%wt., is about the same as the catalytic activity (represented by curve **112**) of a CeO_2 supported, pyrophoric CuO/CeO_2 WGS reaction catalyst.

Similarly, low-pyrophoricity $Pt/CeO_2/Al_2O_3$ WGS reaction catalysts containing reducible metal oxide (CeO_2) loadings of less than 25%wt. also show comparable or higher catalytic activity than the catalytic activity of pyrophoric Pt/CeO_2 WGS reaction catalysts that contain higher amounts of reducible metal oxide. For example, low-pyrophoricity WGS reaction catalysts with catalytically effective loadings of a catalytic agent (Pt) corresponding to column **412** has a reducible metal oxide loading of less than 25%wt. and retain a WGS reaction catalytic activity shown by curve **431** (**Figure 4**). The WGS reaction catalytic activity of the low-pyrophoricity WGS reaction catalyst is comparable to the metal oxide (CeO_2) supported, pyrophoric WGS reaction catalyst, the Pt/CeO_2 WGS reaction catalyst of curve **212** in **Figure 2**. The catalytic activity of the low-pyrophoricity WGS reaction catalysts of the invention as measured by T(50) for the

WGS reaction is about 225 °C in the Pt/CeO$_2$/alumina embodiment shown in **Figure 4**. By comparison, referring to **Figure 2**, the T(50) for the pyrophoric Pt/CeO$_2$ WGS reaction catalyst of curve **212** is about 225 °C.

In some embodiments of the invention, it has also been discovered that preparation of low-pyrophoricity WGS reaction catalysts wherein the catalytic agent is Pt or an thereof, are preferably prepared by impregnation of a suitable support using the Pt-amine salt.

Parameters that are particularly likely to affect the activity of the WGS reaction catalysts of the invention include not only the composition of the catalyst, such as the loading levels of the catalytic agent and metal oxides in the support, but also the reaction process conditions. Conditions that can be varied to optimize the water-gas shift (WGS) reaction, as understood in the art, can also include, but are not limited to, the composition and space velocity of the reactant gas stream, inlet temperature, and the temperature of the WGS reaction catalyst. Water-gas shift reaction catalysts have been extensively studied. For example, Jacques Barbier and Daniel Duprez, Applied Catalysis B: Environmental 4 (1994) 105-140; "Steam effects in three way catalysts" reviews the water-gas shift reaction using a variety of catalytic systems, including systems comprising an alumina support, a CeO$_2$ promoter and a variety of catalytic metals such as platinum, rhodium, and palladium. Accordingly, it is understood in the art from this reference and others that thermodynamic and kinetic considerations dictate the desirability of operating the water-gas shift reaction at temperatures as close to a certain threshold temperature as possible to maximize the conversion of CO to CO$_2$.

Preferably, the water-gas shift reaction process is carried out in a continuous mode with the reactants being passed over a plurality of catalyst particles contained in one or more reaction zones. Gaseous hourly space velocities of at least 500 to about 50,000 hr^{-1} VHSV measured on the basis of dry gas under standard conditions are particularly suitable for most fuel cell operations. However, any suitable gaseous hourly space velocities, as recognized in the art, may be employed.

According to the present invention, carbon monoxide is reacted with steam to produce hydrogen and carbon dioxide. The reactant stream may contain other components besides CO and steam (H$_2$O). In some embodiments, the reactant stream can be a hydrogen containing gas stream mixed with CO and steam and the water-gas

shift reaction can be used to remove CO from the gas stream and simultaneously increase the hydrogen concentration in the gas stream. Often the reactant stream contains at least 10% by volume hydrogen. In some embodiments, the reactant can be received from the products of other reactions which produce compounds such as CO or CO_2 from gas

5   reforming reactions used to oxidize hydrocarbons. The reactant can be admixed with hydrogen, carbon dioxide, steam or nitrogen, as well as minor amounts of olefins, alcohols, aldehydes and/or other hydrocarbons. Preferably, the reactant stream comprises not more than 4-5%v hydrocarbons, not more than 10% CO by volume and not more than 25% CO_2 by volume.

10   In preferred embodiments, the WGS reaction catalysts and methods of the invention are suited for use with a gaseous sample, for example, a hydrogen gas stream comprising CO and steam (H_2O), at a pressure of at least 1 atmosphere and CO of up to 10% by volume. Typically, molar excesses of steam are used relative to the amount of carbon monoxide introduced into the reaction stream. Generally, H_2O:CO molar ratios

15   of between 1:1 (i.e., "1.0") and 20:1 (i.e. "20.0") are preferred in an inlet gas stream before contact with the catalyst, with higher ratios being particularly preferred.

       In preferred embodiments of the present invention, the carbon monoxide and steam containing reactant stream can be passed over the water-gas shift reaction catalyst at temperatures varying between about 150 °C and 600 °C, preferably at temperatures

20   ranging from 175 °C to 350 °C, with the temperature of the reaction mixture in contact with the WGS reaction catalyst being maintained above the dew point temperature of the reaction mixture. Reaction zone pressure is maintained below the dew point pressure of the reaction mixture. It should be recognized that lower or higher reaction zone pressures can be used such as from atmospheric up to about 500 psig. As noted earlier,

25   this process is particularly effective when the feed stock contains 10% or less CO with a molar excess of water vapor. Preferably, the feed stock contains between 1-10% by volume CO using catalysts containing copper and its oxides as a catalytic agent, and between about 0.1-5% by volume CO using catalysts containing Pt and its oxides as a catalytic agent. Preferably, the feed stock contains at least 10% by volume H_2O.

30   As noted above, one skilled in the art would recognize that lower gas reactant flow rates favor more complete CO conversion. Adding more steam or lowering the reaction temperature lowers the equilibrium CO value which can be conceivably be

reached. Accordingly, one of skill in the art would be able to balance theoretical considerations pertaining to reaction design with practical considerations relevant to a particular application so as to optimize parameters to achieve the best possible desired result.

5   The carbon monoxide containing reaction stream should preferably not contain amounts of sulfur or halogens such as chlorine, which can poison and deactivate the catalysts of the invention. Preferably, the levels of sulfur and chlorine in the reactant are kept to below 0.1 ppm in the reactant stream that contacts the catalyst.

        Particularly preferred catalysts of the invention convert carbon monoxide to

10   carbon dioxide, wherein the CO is present in a reaction gas stream, for example, at concentrations of about 10% CO. Typical reaction gas streams can comprise about 30 to 70% hydrogen and water vapor. Using preferred WGS reaction catalysts and methods of the invention, CO concentrations down to about 1,000 ppm or lower can be attained by optimization of the reaction process parameters. One preferred WGS reaction catalyst

15   composition comprises catalytic alumina support particles impregnated with about 8% CuO by weight and about 20% CeO_2 by weight. A particularly preferred catalyst, especially for the low temperature water-gas shift reaction, comprises alumina support particles impregnated with about 8%wt. CuO, about 15 %wt. CeO_2, and about 2.5-5%wt. Cr_2O_3. Another particularly preferred catalyst for the low temperature water-gas shift

20   reaction comprises alumina support particles impregnated with about 8%wt. CuO, and about 2.5-5%wt. of Cr_2O_3.

        Another preferred WGS reaction catalyst composition comprises catalytic alumina support particles impregnated with about 1% Pt by weight and about 25% CeO_2 by weight.

25   A particular advantage of the catalysts of the invention is the ease with which the catalysts can be activated. For example, the catalysts can be activated by passing a reducing gas, such as hydrogen or the process gas itself over the catalyst bed when the catalyst is heated to the operating temperature. Preferably, the process gas, comprising CO and H_2O, serves as the reducing gas. Due to their low-pyrophoricity the activation of

30   the catalysts of the invention does not require the slow, stepwise activation techniques necessary for safe activation of pyrophoric catalysts. Likewise, the reduced catalysts of the invention do not require lengthy passivation procedures prior to exposure to air or during its discharge from the reactor. A particularly advantageous feature of the

invention is that unlike many previous WGS catalysts, the low-pyrophoricity WGS reaction catalysts of the invention can be regenerated subsequent to an exposure to the atmosphere without loss of catalytic activity.

Preferably, the invention is practiced using high strength supports. **Figure 5** shows the mechanical strength of the supports of the invention as measured by crush strength testing. Specifically, **Figure 5** shows a graph **500** comprising an ordinate **510** (y-axis) labeled in units of crush strength (lbs./in^2) and an abscissa **520** (x-axis) showing three types of supports: the supports of the invention as exemplified by alumina particles **521** in a first column **511**, and comparative data for extrudate support preparations as exemplified in a second column **512** for CeO_2/ZrO_2 extrudate support **522** preparations and in a third column **513** for CeO_2 extrudate preparations **523**. The crush strength measurements for columns **511**, **512** and **513** represent an average of 20 measurements collected by applying increasing force on a support particle until it crumbles and recording the corresponding force per unit area as the "crush strength". The supports of the invention offer 2 to 10 times the mechanical strength of the tested extrudate prepared supports that are also used as catalyst supports in the art.

The WGS reaction catalyst can be used in various types of process configurations. **Figure 6** illustrates one preferred embodiment wherein a system **600** comprises WGS reaction catalysts of the invention configured as upstream catalysts in a gas process stream for lowering the CO concentration in a hydrogen stream. **Figure 6** shows a schematic diagram of a system **600** for reducing the concentration of CO in a reactant **610** gas stream. The system comprises a gas stream contained in a containment surface **601**, a first catalytic region **620**, an intermediate gas stream **630**, a second catalytic region **640** and a product **650** gas stream. The reactant **610** gas stream can, for example, contain a test gas composition of about 8%v CO, about 25%v water vapor and about 35%v hydrogen in a nitrogen stream at a total pressure of about 1 atmosphere. The reactant **610** gas stream flows through the first catalytic region **620**, where it flows through a plurality of first WGS reaction catalyst particles **621**. In one embodiment, the first WGS reaction catalyst particles **621** are CuO and CeO_2 impregnated 1/8-inch cross section alumina support particles which catalyze the water-gas shift reaction. The space velocity of the reactant **610** gas stream and temperature of the first catalytic region **620** can be set to optimize the catalysis of the water-gas shift reaction and minimize the concentration of CO in the intermediate gas stream **630**. Preferably for the catalysts and

apparatus of the invention, the space velocity is at least 500 hr^{-1}. For example, one

skilled in the art would recognize that a temperature of about 175 °C, preferably at least

200 °C, and a VHSV of about 2,500 hr^{-1} are likely to maximize the CO conversion of a

$CuO/CeO_2/Al_2O_3$ WGS reaction catalyst. WGS reaction catalyst temperatures below

5   about 175 °C are unlikely to adequately catalyze the water-gas shift reaction. In contrast,

the $CuO/Cr_2O_3/CeO_2/Al_2O_3$ or $CuO/Cr_2O_3/Al_2O_3$ catalysts of the invention, are quite

active at 175 °C, however. Other operating conditions, as recognized in the art, are of

course also possible and even desirable for certain applications.

The intermediate gas stream **630** then enters the second catalytic region **640**,

10   where it flows through a plurality of second WGS reaction catalyst particles **641**. In one

embodiment, the second WGS reaction catalyst particles **641** are Pt and CeO_2

impregnated 1/8-inch cross section alumina particles which catalyze the water-gas shift

reaction. The space velocity of the intermediate gas stream **630** gas stream and

temperature of the second catalytic region **640** can be set to optimize the water-gas shift

15   reaction and minimize the concentration of CO in the product **650** gas stream. Preferably

for the catalysts and apparatus of the invention, the space velocity is at least 500 hr^{-1}.

For example, one skilled in the art would recognize that a temperature of about 200 °C

and a VHSV of about 1,000 hr^{-1} are likely to maximize the CO conversion of such a

$Pt/CeO_2/Al_2O_3$ catalytic system. As understood in the art, the optimal space velocity can

20   be related to the level of CO in the reactant **610** gas stream. For instance, at CO

concentrations up to 3%v, VHSV's of between 1,000 and about 6,000 hr^{-1} across the

$Pt/CeO_2/Al_2O_3$ WGS reaction catalysts of the second WGS reaction catalysts **641** of the

invention typically result in CO concentration in the product **650** gas stream of about

0.3%v. Higher space velocities through the system are also within this embodiment, for

25   example space velocities of about 6,000 hr^{-1} VHSV up to about 30,000 hr^{-1} VHSV may

also be desired through the system. Catalyst temperatures below about 175 °C are

unlikely to adequately catalyze the water-gas shift reaction for this particular catalyst.

Enhanced WGS reaction catalytic activity is favored by using a high surface area

alumina support beads, for example with a BET surface area of at least 10 m^2/g,

30   preferably at least 200 m^2/g. The size of the support particles typically affects the

pressure drop across catalytic regions, with larger particles leading to lower pressure

drop while potentially limiting the gas stream conversion by the rate of gas diffusion,

while smaller support particles can create larger backpressure thereby potentially limiting the flow of a gas stream by increasing the pressure drop across the catalytic region. Any appropriate method of packing or preparing the WGS reaction catalysts of the invention can be selected by one skilled in the art to prepare a catalytic system to practice the

5 invention. Other operating parameters, as recognized in the art, are of course also possible and even desirable for certain applications.

Apparatus of the invention include reactors containing catalyst beds (having the low-pyrophoricity WGS reaction catalysts) for carrying out the water-gas shift reaction. The apparatus, for example, can be used to generate hydrogen to power a fuel cell. The

10 apparatus can also be used in other applications where hydrogen generation is desired. Additionally, the apparatus can be used to reduce CO concentrations in gas streams.

The WGS reaction catalysts of the present invention have utility for many other uses where hydrogen generation is desired, including hydrogen gas generation, uses with alcohol or ammonia synthesis, Fischer Tropsch synthesis, and the like. For example, the

15 WGS reaction catalysts and methods of the invention can be used to replace conventional high temperature iron-chromium based WGS reaction catalysts such as Fe_2O_3/Cr_2O_3 that typically operate at about 350 °C, as well as conventional low temperature copper-zinc based catalysts such as $CuO/ZnO/Al_2O_3$ which typically operate at about 200 °C.

The following examples further illustrate the present invention, but of course,

20 should not be construed as in any way limiting its scope.

Example 1: Preparation of a CuO/CeO_2/alumina low-pyrophoricity WGS reaction catalyst

To prepare a WGS reaction catalyst wherein the support is alumina, the reducible

25 metal oxide is ceria and the catalytic agent is CuO, ceria impregnated alumina support particles were prepared by incipient wetness impregnation of alumina beads or particulates.

1/8-inch alumina support particles (ALCOA DD-443) were dried for 2 hours at 200 °C and then calcined for 2 hours at 500 °C. The calcined 1/8-inch particles were

30 then impregnated (i.e., impregnated at 55% incipient wetness to obtain about 14% CeO_2) in an aqueous solution of cerium nitrate (i.e., $Ce(NO_3)_3$, used 1.7 g/cc, 28.5% REO; 57.8 g ceria dissolved in 22 g water, per 100 g alumina). The particles were then dried at 120

°C for 8 hours and impregnated a second time (i.e. impregnation at 45% incipient wetness to obtain about 25% CeO_2) in a $Ce(NO_3)_3$ aqueous solution (i.e., 57.8 g $Ce(NO_3)_3$ in 18.5 g deionized water for 116.8 g ceria impregnated alumina). The sample was then calcined at 500 °C for 2 hours.

5   The ceria/alumina particles were impregnated (i.e., impregnated at 44% incipient wetness to obtain 8% CuO) with Cu-nitrate solution (i.e., 26.6 mL of 5M $Cu(NO_3)_2$ solution in 32 mL deionized water) at a pH of 6, dried at 120 °C for 8 hours and then calcined at 500 °C for 2 hours to prepare CuO/ceria/alumina WGS reaction catalysts.

10   Example 2: Preparation of a $CuO/Cr_2O_3/CeO_2$/alumina low-pyrophoricity WGS reaction catalyst (8%wt. CuO, 2%wt. Cr_2O_3, 15%wt. CeO_2)

       Alcoa DD-443 alumina 1/8" spheres at 500 °C were calcined for 2 h for a total surface area of approximately 220-240 m^2/g. The incipient wetness volume was determined (i.e. 0.52 mL/g). The calcined alumina spheres were impregnated with cerium nitrate solution to incipient wetness. The concentration of the cerium nitrate

15   solution was adjusted to achieve a 5%wt. loading of CeO_2 after drying and calcination. (For example, 100 g alumina can be impregnated with 10.75 mL of a solution containing 28.8%wt. cerium nitrate and a density of 1.7 g/mL mixed with 41.25 mL water.) The impregnated spheres were dried at 120 °C for 8 h, and calcined at 500 °C for 4 h. The

20   CeO_2/alumina spheres were impregnated to incipient wetness with $Cr(NO_3)_3$ solution. The concentration of the $Cr(NO_3)_3$ solution was adjusted to achieve a 6%wt. loading of Cr_2O_3 after drying and calcination. (For example 100 g of the support material can be impregnated with 42 mL of 2 M $Cr(NO_3)_3$ solution diluted with water to the incipient wetness volume.) The impregnated spheres were dried at 120 °C for 8 h, and calcined at

25   500 °C for 4 h. The Cr_2O_3/CeO_2/alumina spheres were impregnated with $Cu(NO_3)_2$ solution. The concentration of $Cu(NO_3)_2$ solution was adjusted to achieve a 8%wt. loading of CuO after drying and calcination. (For example, for 100 g of support material, 22 mL of 5 M $Cu(NO_3)_2$ solution was diluted with water to the incipient wetness volume of the support.) The impregnated spheres were dried at 120 °C for 8 h,

30   and calcined at 500 °C for 4 h.

Example 3: Preparation of a Pt/CeO$_2$/alumina low-pyrophoricity WGS reaction catalyst

To prepare a WGS reaction catalyst wherein the support is alumina, the reducible metal oxide is ceria and the catalytic agent is Pt, ceria impregnated alumina support particles were prepared by incipient wetness impregnation of alumina beads or

5   particulates.

1/8-inch alumina support particles (ALCOA DD-443) were dried for 2 hours at 200 °C and then calcined for 2 hours at 500 °C. The calcined 1/8-inch particles were then impregnated (i.e., impregnated at 55% incipient wetness to obtain about 14% CeO$_2$) in an aqueous solution of cerium nitrate (i.e., Ce(NO$_3$)$_3$, used 1.7 g/cc, 28.5% REO; 57.8

10   g ceria dissolved in 22 g deionized water, per 100g alumina). The particles were then dried at 120 °C for 2 hours and impregnated a second time (i.e. impregnation at 45% incipient wetness to obtain about 25% CeO$_2$) in a Ce(NO$_3$)$_3$ aqueous solution (i.e., 57.8 g Ce(NO$_3$)$_3$ in 18.5 g deionized water for 116.5 g ceria impregnated alumina). The sample was then calcined at 500 °C for 2 hours.

15   The ceria/alumina particles were impregnated (i.e., impregnated at 44% incipient wetness to obtain 0.5% Pt) with Pt-amine solution (i.e., 3.7 g Pt-amine and 55.6 g. deionized water were used for 133 g ceria/alumina) at a pH of 6.

Impregnation of ceria/alumina particles with the water soluble Pt-amine salt solution, was followed by precipitation with acetic acid, drying at 120 °C for 8 hours and

20   calcination at 500 °C for 4 hours to prepare Pt/ceria/alumina WGS reaction catalysts of the invention.

Example 4: Composition of low-pyrophoricity CuO/CeO$_2$/alumina WGS reaction catalysts

25   The experimental data for **Table 1**, which is illustrated in **Figure 3**, was collected using a multi-tube reactor (1/4-inch diameter stainless steel tubes) and granular samples (0.3 to 0.7 mm particle size, diameter) at 200 mg sample per tube and 0.1 SLPM dry flow per tube. Experimental error caused by temperature gradients may be as large as 10%. Activity is expressed as the temperature needed to reach 50% conversion (i.e.,

30   T(50)). The lower the temperature (the higher the data point), the better the activity of the WGS reaction catalyst. The reactant stream used was a nitrogen stream containing

2%v CO, 20%v hydrogen and 10%v H_2O at a VHSV of 30,000 hr^{-1}. The optimum CuO loading was at about 8%. The optimum CeO_2 loading was 10-15%.

Table 1

Trial	CeO₂ loading (%wt.)	CuO loading (%wt.)	T(50) in °C
1	5	4	350
2	5	8	190
3	5	12	180
4	10	4	230
5	10	8	170
6	10	12	180
7	15	4	350
8	15	8	225
9	15	12	225
10	20	4	330
11	20	8	218
12	20	12	205

Example 5: Preferred Composition of $CuO/Cr_2O_3/Al_2O_3$ and $CuO/Cr_2O_3/CeO_2/Al_2O_3$ WGS reaction catalysts

The experimental data for the $CuO/Cr_2O_3/Al_2O_3$ and $CuO/CuO/Cr_2O_3/CeO_2/Al_2O_3$ WGS reaction catalysts, was collected using a quartz-tube reactor (1 inch diameter) and granular samples (1/8 inch) at 16 g of sample per tube . Activity is expressed as the temperature needed to reach 50% conversion (i.e., T(50)). The lower the temperature (the higher the data point), the better the activity of the WGS reaction catalyst. The reactant stream used was a nitrogen stream containing 8%v CO, 10%v CO_2, 43%v hydrogen (dry gas) and 26%v H_2O at a VHSV of 2,500 hr^{-1} (wet).

The experimental data for the $CuO/Cr_2O_3/Al_2O_3$ WGS reaction catalysts is presented **Table 2**. Complete conversion temperature curves for these WGS reaction catalysts are illustrated in **Figure 7**.

Table 2

Composition (%wt.)	T(50) (°C)
8% CuO/Al_2O_3	214
8% $CuO/2\%\ Cr_2O_3/Al_2O_3$	173
8% $CuO/8\%\ Cr_2O_3/Al_2O_3$	168

The experimental data for the $CuO/Cr_2O_3/CeO_2/Al_2O_3$ WGS reaction catalysts is presented **Table 3**. Complete conversion temperature curves for these WGS reaction

5   catalysts are illustrated in **Figure 8**.

Table 3

Composition (%wt.)	T(50) (°C)
8% $CuO/15\%\ CeO_2/Al_2O_3$	215
8% $CuO/2.1\%\ Cr_2O_3/15\%\ CeO_2/Al_2O_3$	175
8% $CuO/5\%\ Cr_2O_3/15\%\ CeO_2/Al_2O_3$	172

10   Example 6: Effect of Sequence of Impregnation/Calcination Steps on Catalytic activity
     of an 8% $CuO/2\%\ Cr_2O_3/15\%CeO_2/Al_2O_3$ Reaction Catalyst

The experimental data for the 8% $CuO/2\%\ Cr_2O_3/15\%CeO_2/Al_2O_3$ WGS reaction catalysts prepared by various sequences of synthetic steps and a comparative WGS reaction catalyst without Cr_2O_3, was collected using a quartz-tube reactor (1 inch

15   diameter) and granular samples (1/8 inch) at 16 g of sample per tube. The various synthetic sequences are described more fully in the Detailed Description. The data is presented in **Table 4**. Complete conversion temperature curves are illustrated in **Figure 9**. Activity is expressed as the temperature needed to reach 50% conversion (i.e., T(50)). The lower the temperature (the higher the data point), the better the activity of the WGS

20   reaction catalyst. The reactant stream used was a nitrogen stream containing 8%v CO, 10%v CO_2, 43%v hydrogen (dry gas) and 26%v H_2O at a VHSV of 2,500 hr^{-1} (wet).

Table 4

Order of Addition of Cr_2O_3 and CuO on 8% CuO/(2% Cr_2O_3)/15%CeO_2/Al_2O_3	T(50) (°C)
no Cr_2O_3	215
Cr_2O_3 added last	215
Cr_2O_3 added first	180
Cr_2O_3 added before CuO, not calcined	180

Example 7: Preferred Composition of Pt/CeO_2/alumina WGS reaction catalysts

The experimental data for **Table 5**, which is illustrated in **Figure 4**, was collected using a quartz-tube reactor (1 inch diameter) and granular samples (1/8 inch) at 10 g of sample per tube . Activity is expressed as the temperature needed to reach 50% conversion (i.e., T(50)). The lower the temperature (the higher the data point), the better the activity of the WGS reaction catalyst. The reactant stream used was a nitrogen stream containing 0.5%v CO, 20%v hydrogen and 10%v H_2O at a VHSV of 24,000 hr^{-1}. The optimum CeO_2 loading was at about 24%.

Table 5

Trial	CeO_2 loading (%wt)	Pt loading (%wt.)	T(50) in °C
1	13	0.37	260
2	25	0.7	220

Example 8: Pyrophoricity Measurements

Method A

Measurements were performed on a Rheometric Scientific instrument. The procedure is as follows:

1. Charge the sample container with 10-30 mg powdered catalyst sample.
2. Heat the sample in a 7% H_2 / N_2 stream to 350 °C at 10 °C / min.
3. Hold at 350 °C for 20 minutes.
4. Switch gas flow to N_2 and cool to 100 °C.
5. Hold at 100 °C for 15 min.

6.   Switch gas flow to air, hold temperature for another 15 minutes.
Purge with nitrogen.

The result is a number for the exotherm in units of [$\mu V*s/mg$], which is directly related

to the released heat ΔH [cal/g] by an unknown conversion factor **F**:

ΔH [cal/g] = **F***[$\mu V*s/mg$]   (1)

The exotherm ΔT [°C] can be calculated from the released heat ΔH [cal/g] by using the

heat capacity of the solid c_p: $\Delta T = \Delta H$ [cal/g] / c_p.   (2)

Thus, $\Delta T =$ **F** * [$\mu V*s/mg$] / c_p.   (3)

Values for c_p can be found in the literature. In order to find the factor **F**, literature

reported values for ΔT and c_p are used for the commercially available materials

($CuO/ZnO/Al_2O_3$; FeCr).

$F = \Delta T*c_p$ / [$\mu V*s/mg$]   (4)

The calculated factor is then used for the unknown materials to calculate ΔT using

equation (3).

Method B

Pyrophoricity was tested using a Differential Scanning Calorimeter measurement.

Measurements were performed on a Rheometric Scientific instrument. The procedure is

as follows:

1.   Charge the sample container with 10-30 mg powdered catalyst sample.

2.   Heat the sample in a 7% H_2 / N_2 stream to 350 °C at 10 °C / min.

3.   Hold at 350 °C for 20 minutes.

4.   Switch gas flow to N_2 and cool to 250 °C.

5.   Hold at 250 °C for 15 min.

6.   Switch gas flow to air, hold temperature for another 15 minutes.
Purge with nitrogen.

The exotherm upon oxidation in step 6 is recorded in units of cal/g. A temperature rise is

calculated from this number by division by C_p [cal/g-K].

The pyrophoricity data measurements in **Table 6** were obtained using Method B.

Table 11

Catalyst	DTA Result	Est. Temp. Rise (°C)	T(50) in °C
FeCr commercial HTS catalyst (Fe$_2$O$_3$/Cr$_2$O$_3$)	57	450	320

Example 14, Comparative Example: Pyrophoricity and activity of Pt/CeO$_2$ WGS

5   catalytic systems

The experimental data for **Table 12**, which is illustrated in **Figure 2**, was collected using alumina particles (1/8-inch diameter) supplied by Alcoa (DD-443; 327 m^2/g BET surface area before calcination). The pyrophoricity data was collected using Method A of Example 8.

10   Catalytic activity is expressed as a CO-conversion temperature curve for all catalysts under identical conditions. The lower the temperature where high conversions are achieved, the higher the activity. The reactant stream used was a nitrogen stream containing 0.5%v CO, 20%v hydrogen and 10%v H$_2$O at a VHSV of 24,000 hr^{-1}.

15   **Table 12**

Catalyst	DTA Result	Est. Temp. Rise (°C)
0.5% Pt/ CeO$_2$	67	400

Example 15: Mechanical Strength of Pt/CeO$_2$/alumina low temperature WGS catalytic systems

Crush strength measurements were performed on an Instrom (Model No. 1123,

20   Serial No. 5376) instrument equipped wth a Microcon data station. Crosshead speed was 0.02 inches/second with a 100 lbs./in^2 force at full scale. The support materials tested were Alcoa alumina spheres (1/8-inch diameter; DD-443), Rhodia NGL-59A (CeO$_2$/ZrO$_2$/Al$_2$O$_3$, 64/26/10) extrudates (0.11-inch diameter, 8-10 mm length) and Rhodia NGL-66A (CeO$_2$/Al$_2$O$_3$, 75/25) extrudates (0.06-inch diameter, 6-8 mm length).

25   All materials were dried at 200 °C and kept in closed containers until measurement. Twenty pieces of each support were measured and the average value as well as the standard deviation was computed. The results are shown graphically in **Figure 5**.

Alumina sphere supports provide about a 2-fold increase in crush strength over CeO_2/ZrO_2 extrudate supports and about a 10-fold increase in mechanical strength over CeO_2 extrudate supports.

5 Example 16: Comparative Example: Mechanical Strength of Pt/CeO₂ low temperature WGS catalytic systems

Assessment of support mechanical strength was made through crush strength measurements performed on an Instrom (Model No. 1123, Serial No. 5376) instrument equipped with a Microcon data station. Crosshead speed was 0.02 inches/second with a

10 100 lbs./in² force at full scale. The support materials tested were Rhodia NGL-59A ($CeO_2/ZrO_2/Al_2O_3$, 64/26/10) extrudates (0.11-inch diameter, 8-10 mm length) and Rhodia NGL-66A (CeO_2/Al_2O_3, 75/25) extrudates (0.06-inch diameter, 6-8 mm length). All materials were dried at 200 °C and kept in closed containers until measurement. Twenty pieces of each support were measured and the average value as well as the

15 standard deviation was computed. The results are shown graphically in **Figure 5**. Alumina sphere supports provide about a 2-fold increase in crush strength over CeO_2/ZrO_2 extrudate supports and about a 10-fold increase in mechanical strength over CeO_2 extrudate supports. CeO_2 extrudates containing various amounts of binder have shown inferior strength to alumina spheres in our qualitative tests.

20

Table 6

Composition	ΔH_{ox} [cal/g]	C_p [cal/g-K]	ΔT [K]
Commercial CuZn (UCI)	124.4	0.201	621.5
8% CuO/15 % CeO$_2$/Al$_2$O$_3$	4.5	0.299	15.04
8% CuO/2% Cr$_2$O$_3$/15% CeO$_2$/Al$_2$O$_3$	11.42	0.299	38.23
8% CuO/2% Cr$_2$O$_3$/Al$_2$O$_3$	12.72	0.267	47.65
12% CuO/2% Cr$_2$O$_3$/10% CeO2/Al$_2$O$_3$	23.0475	0.248	92.68
12% CuO/2% Cr$_2$O$_3$/5% CeO2/Al$_2$O$_3$	31.406	0.257	122.19
12% CuO/2% Cr$_2$O$_3$/15% CeO$_2$/Al$_2$O$_3$	26.97	0.239	112.68

Example 9: Pyrophoricity and activity of low-pyrophoricity CuO/CeO$_2$/alumina WGS reaction catalysts

The experimental data for **Table 7**, which is illustrated in **Figure 1**, was collected using alumina particles (1/8-inch diameter) available from Alcoa (DD-443; 327 m^2/g BET surface area before calcination). The pyrophoricity data was collected using Method A of Example 8.

Catalytic activity is expressed as a CO-conversion temperature curve for all WGS reaction catalysts under identical conditions. The lower the temperature where high conversions are achieved, the higher the activity. The reactant stream used was a nitrogen stream containing 2.0%v CO, 20%v hydrogen, 10%v H$_2$O and 5%v CO$_2$ at a VHSV of 5,000 hr^{-1}.

Table 7

Catalyst	DTA Result $\mu V.s/mg$	Est. Temp. Rise (°C)	T(50) in °C
8% CuO/20% CeO$_2$/Al$_2$O$_3$	43.04	100	210

Example 10: Pyrophoricity and activity of Pt/CeO$_2$/alumina low-pyrophoricity WGS catalytic systems

The experimental data for **Table 8**, which is illustrated in **Figure 2**, was collected using alumina particles (1/8-inch diameter) supplied by Alcoa (DD-443; 327 m^2/g BET surface area before calcination). The pyrophoricity data was collected using Method A of Example 8.

5   Catalytic activity is expressed as a CO-conversion temperature curve for all WGS reaction catalysts under identical conditions. The lower the temperature where high conversions are achieved, the higher the activity. The reactant stream used was a nitrogen stream containing 0.5%v CO, 20%v hydrogen and 10%v H_2O at a VHSV of 24,000 hr^{-1}.

10

Table 8

Catalyst	DTA Result μV.s/mg	Est. Temp. Rise (°C)	T(50) in °C
0.5%wt. Pt/ 20%wt. CeO$_2$/alumina	8.4	50	210

Example 11, Comparative Example: Pyrophoricity and Activity of CuO/CeO$_2$ WGS

15   reaction catalyst

      The experimental data for **Table 9**, which is illustrated in **Figure 1**, was collected using using a CuO/CeO$_2$ based WGS reaction catalyst. The pyrophoricity data was collected using Method A of Example 8.

      Catalytic activity is expressed as a CO-conversion temperature curve for all

20   catalysts under identical conditions. The lower the temperature where high conversions are achieved, the higher the activity. The reactant stream used was a nitrogen stream containing 2.0%v CO, 20%v hydrogen, 10%v H_2O and 5%v CO_2 at a VHSV of 5,000 hr^{-1}.

25   **Table 9**

Catalyst	DTA Result μV.s/mg	Est. Temp. Rise (°C)	T(50) in °C
7.5% CuO/CeO$_2$	103	600	220

Example 12, Comparative Example: Pyrophoricity and Activity of copper/zinc based low temperature WGS reaction catalyst

The experimental data for **Table 10**, which is illustrated in **Figure 1**, was

5   collected using a commercially available copper/zinc based low temperature WGS reaction catalyst from United Catalysts (UCI). Typical copper/zinc based low temperature WGS reaction catalysts contain about 33%wt. CuO, about 35-55%wt. ZnO, with the balance %wt. being Al_2O_3 (Catalyst Handbook; Twigg, M.V., Ed.; Wolfe Publishing, 1989, p 312). The pyrophoricity data was collected using method A of

10 Example 8.

Catalytic activity is expressed as a CO-conversion temperature curve for all catalysts under identical conditions. The lower the temperature where high conversions are achieved, the higher the activity. The reactant stream used was a nitrogen stream containing 2.0%v CO, 20%v hydrogen, 10%v H_2O and 5%v CO_2 at a VHSV of 5,000 hr⁻

15 ¹.

Table 10

Catalyst	DTA Result $\mu V.s/mg$	Est. Temp. Rise (°C)	T(50) in °C
Cu/Zn commercial LTS catalyst	177	800	160

20 Example 13, Comparative Example: Pyrophoricity and Activity of iron/chromium based high temperature WGS reaction catalyst

The experimental data for **Table 11**, which is illustrated in **Figure 1**, was collected using commercially available iron/chromium based WGS catalyst. The pyrophoricity data was collected using Method A of Example 8.

25 Catalytic activity is expressed as a CO-conversion temperature curve for all catalysts under identical conditions. The lower the temperature where high conversions are achieved, the higher the activity. The reactant stream used was a nitrogen stream containing 2.0%v CO, 20%v hydrogen, 10%v H_2O and 5%v CO_2 at a VHSV of 5,000 hr⁻

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